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U.S. ARMY RESEARCH, DEVELOPMENT AND ENGINEERING COMMAND

Aberdeen Proving Ground, MD 21010-5424

INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY: SAMPLE ANALYSIS OF ZIRCONIUM AND RUTHENIUM IN METAL ORGANIC FRAMEWORKS

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14. ABSTRACT:
The Forensic Analytical Center at the U.S. Army Edgewood Chemical Biological Center (Aberdeen Proving Ground, MD) was recently requested to analyze metal organic frameworks (MOFs) using inductively coupled plasma mass spectrometry (ICP–MS). Specifically, the MOFs were analyzed for the zirconium-to-ruthenium ratios. The ability to process MOFs for specific elemental components allows scientists to modify the MOF structures to sequester chemicals through adsorption and hydrogen bonding.

15. SUBJECT TERMS

Metal organic framework (MOF)	Ruthenium
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PREFACE

The work described in this report was started in August 2016 and completed in August 2017.

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INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY: SAMPLE ANALYSIS OF ZIRCONIUM AND RUTHENIUM IN METAL ORGANIC FRAMEWORKS

1.   INTRODUCTION

The Forensic Analytical Center (FAC) at the U.S. Army Edgewood Chemical Biological Center (ECBC; Aberdeen Proving Ground, MD) has developed an analytical method for investigating metal organic frameworks (MOFs) using inductively coupled plasma mass spectrometry (ICP–MS). Specifically, MOFs were analyzed for Zr-to-Ru ratios. ICP–MS has the ability to detect elements from subpart-per-trillion to percent-level concentrations. This ability to process MOFs for specific elemental components allows scientists to modify MOF structures to sequester chemicals through adsorption and hydrogen bonding.

2.   BACKGROUND

A central mission of the ECBC FAC is to develop and validate quantitative analytical methods, with a focus on those methods addressing elemental analysis of materials. ECBC's forensic capabilities were originally developed to support U.S. obligations under the Chemical Weapons Convention, whereby the United States was required to develop sampling and analysis expertise to verify treaty compliance. The ECBC FAC is accredited in accordance with the ISO/IEC 17025 standard that refers to laboratory operations and quality control.[1] Demonstrating ECBC's high standards in chemical and biological agent detection and analysis, the ECBC FAC maintains elite status in international proficiency testing sponsored by the Organisation for the Prohibition of Chemical Weapons (The Hague, Netherlands).

Traditionally, activated carbons have been used for the removal of highly toxic chemicals; however, to achieve a broad spectrum of protection, activated carbons must be impregnated with a variety of compounds that are capable of both acid and base chemistries.[2] Impregnating carbon atoms with other compounds causes the chemical groups to interact, which decreases the efficacy of the material over time. Research has focused on the covalent anchoring of functional groups to the substrate through the crystal designs of MOFs. MOFs are clusters of metal ions that are linked together. Because MOFs are highly porous with larger surface areas, they have been increasingly popular for investigating gas sorption chemistry.

The Agilent 7900 ICP–MS system (Agilent Technologies; Santa Clara, CA) has a plasma and Ultra High Matrix Introduction accessory that operates at more than 100 times the traditional matrix limit for ICP–MS technology.[3] The samples were prepared using microwave digestion in an acid solution followed by dilution with water. The matrix of the samples analyzed was 3% HNO_3 with 0.1% HCl. After digestion, 50 µL of HF was added to each sample to keep the Zr in solution.

3.   MATERIALS AND METHODS

3.1   Materials

Laboratory-grade chemicals from any supplier are appropriate for this procedure. The following chemicals were used:

- liquid argon (dewar);
- helium (tank);
- hydrogen (tank);
- double-distilled or 18 MΩ water that was free of metals;
- concentrated HNO_3, HCl, and HF, of a minimum trace-metal grade or grade that was suitable for the intended detection level; and
- tuning solution of 1 ppm Ce, Co, Li, Tl, and Y.

The following common laboratory equipment and supplies were used:

- analytical balance with readability of 0.001 mg;
- disposable plastic droppers;
- polypropylene (PP) bottles or perfluoroalkoxy bottles when available;
- PP graduated cylinders or equivalent;
- PP Falcon tubes, 15 mL and 50 mL or equivalent;
- pipetters and disposable tips covering the range of 10 µL to 10 mL;
- waste container;
- laboratory cleaning wipes; and
- glass microslides.

The following specialized equipment and supplies were used:

- 7900 Series ICP–MS system (part no. G8403A; Agilent Technologies);
- ICP–MS MassHunter workstation (part no. G7215C with #003; Agilent Technologies);
- Cetac ASX-500 auto sampler (part no. G3286A; Cetac Technologies; Omaha, NE);
- CEM Discover SP-D digestion system (part no. 7746-22110; CEM Corporation; Matthews, NC);
- 1000 µg/mL Zr in 3% HNO_3 (CAS no. 7440-67-7; part no. CGZR1-125ML; Inorganic Ventures; Christiansburg, VA); and
- 1000 µg/mL Ru in 3% HNO_3 (CAS no. 7440-18-8; part no. CGRU1-125ML; Inorganic Ventures).

3.2 Methods

3.2.1 Preparation of the Matrix Solution

Note: All stock solutions and the dilutions from those stock solutions must be remade every 3 months unless a stability study is performed that shows a longer storage time is acceptable. Store all solutions at ambient temperatures.

Solutions were prepared as follows: Fill a PP, 1 L volumetric flask, or HDPE bottle approximately half-full with water. Add 30 mL of concentrated HNO_3 and swirl. Adjust final volume or weight for the flask or bottle to 1 L or 1000 g, respectively, with water, for a 3% solution. Table 1 lists the solvent matrix and rinse solution recipes.

Table 1. Solvent Matrix and Rinse Solution

Solution Name and Final Concentration (1 L)	Amount To Be Added to PP Volumetric Flask
1% HNO_3, 0.1% HCl	10 mL of concentrated HNO_3 100 µL of HCl Double-distilled or 18 MΩ H_2O
3% HNO_3, 0.1% HCl	30 mL of concentrated HNO_3 100 µL of HCl Double-distilled or 18 MΩ H_2O
5% HNO_3, 0.1% HCl	50 mL of concentrated HNO_3 100 µL of HCl Double-distilled or 18 MΩ H_2O

Note: Always add acid to water.

3.2.2 Preparation of Stock Standard Solutions

The standard solutions (Table 2) were made in 15 mL PP tubes. Dilutions of the standard solutions were prepared by pipetting the solvent of diluted HNO_3 plus HCl into a tube and then pipetting the standard solution. Note that the solvent should match the acid composition and concentration that was used for the sample preparation. Ideally, the standards and samples will have the same percentages of acids in them. This allows for the same amount of sample to be introduced from the nebulizer to the detector and thereby minimizes matrix effects.

The indicated amount of stock solution was added to the tube with a volumetric pipette. The remaining volume of solvent (3% HNO_3, 0.1% HCl) was pipetted to make a total volume of 10 mL.

Table 2. Dilution Instructions for Calibration Standards

Solution Name	Final Concentration (µg/mL)	Amount to Be Added to 15 mL PP Tube
Level 1	10	0.100 mL of Zr, 0.100 mL of Ru, 9.80 mL of 3% HNO_3 + 0.1% HCl, 20 µL of HF
Level 2	2	2 mL of Level 1, 8 mL of 3% HNO_3 + 0.1% HCl, 20 µL of HF
Level 3	1	1 mL of Level 1, 9 mL of 3% HNO_3 + 0.1% HCl, 20 µL of HF
Level 4	0.2	200 µL of Level 1, 9.8 mL of 3% HNO_3 + 0.1% HCl, 20 µL of HF
Level 5	0.1	100 µL of Level 1, 9.9 mL of 3% HNO_3 + 0.1% HCl, 20 µL of HF
Level 6	0.05	50 µL of Level 1, 9.95 mL of 3% HNO_3 + 0.1% HCl, 20 µL of HF
Level 7	0.01	100 µL of Level 3, 9.9 mL of 3% HNO_3 + 0.1% HCl, 20 µL of HF
MDL	0.005	50 µL of Level 3, 9 mL of 3% HNO_3 + 0.1% HCl, 20 µL of HF

MDL, method detection limit.

3.2.3 Quality Assurance Samples

For the method blank, a sample of 3% HNO_3 (from the same lot) was processed through the entire sample preparation procedure with each batch of samples. The method blank was then analyzed with the samples.

For the reagent blank, a sample of 3% HNO_3 and 0.1% HCl was run after each continuing calibration verification sample and each sample to ensure that no carryover occurred.

3.2.4 Sample Analysis

To prepare the instrument for analysis, necessary performance verification was completed in accordance with WI-091.[4] Fresh 5% HNO_3, 0.1% HCl solutions were added to 15 mL PP tubes; fresh 3% HNO_3, 0.1% HCl solutions were added to 15 mL PP tubes; and fresh 1% HNO_3, 0.1% HCl solutions were added to 15 mL PP tubes. These three solutions served as rinses, and a set was required between each sample. Tubing was changed as necessary. The calibration curve samples, unknown samples, and quality MOF samples were loaded into the auto sampler, and the sequence was run.

4. RESULTS AND DISCUSSION

4.1 Calibration Curves

Qualitative analyses of the analytes in the solutions were determined by the presence of a signal for the most abundant isotope of a given element. Interferences of major isotopes were minimized by running the collision reaction cell in no-gas (no. 1), helium gas (no. 2), and hydrogen gas (no. 3) modes. The major ions were analyzed under all no-gas modes. Quantitative analysis of analytes in solution was performed by generating a five-point calibration

curve and forcing the intercept through zero. Equation 1 was used to convert the signal into a concentration using the slope and intercept of the calibration curve:

$$Y = \frac{(A/S) - B}{M} \tag{1}$$

where Y is the measured concentration (in ppm), A is the signal of the analyte, S is the signal of the standard, B is the y intercept, and M is the slope of the calibration curve.

The measured concentration was converted to a final concentration by multiplying by a dilution factor as shown:

$$C_f = C_M \times (V_f / V_s) \tag{2}$$

where C_f is the final concentration (in ppm), C_M is the measured concentration (in ppm), V_f is the final volume of the solution analyzed, and V_s is the volume of the sample.

Concentrations used in this study were optimized to produce linear regression fits for the calibration curves. The goodness of the linear fits are summarized in Table 3 and Figure 1.

Table 3. Concentration Range for Each Analyte

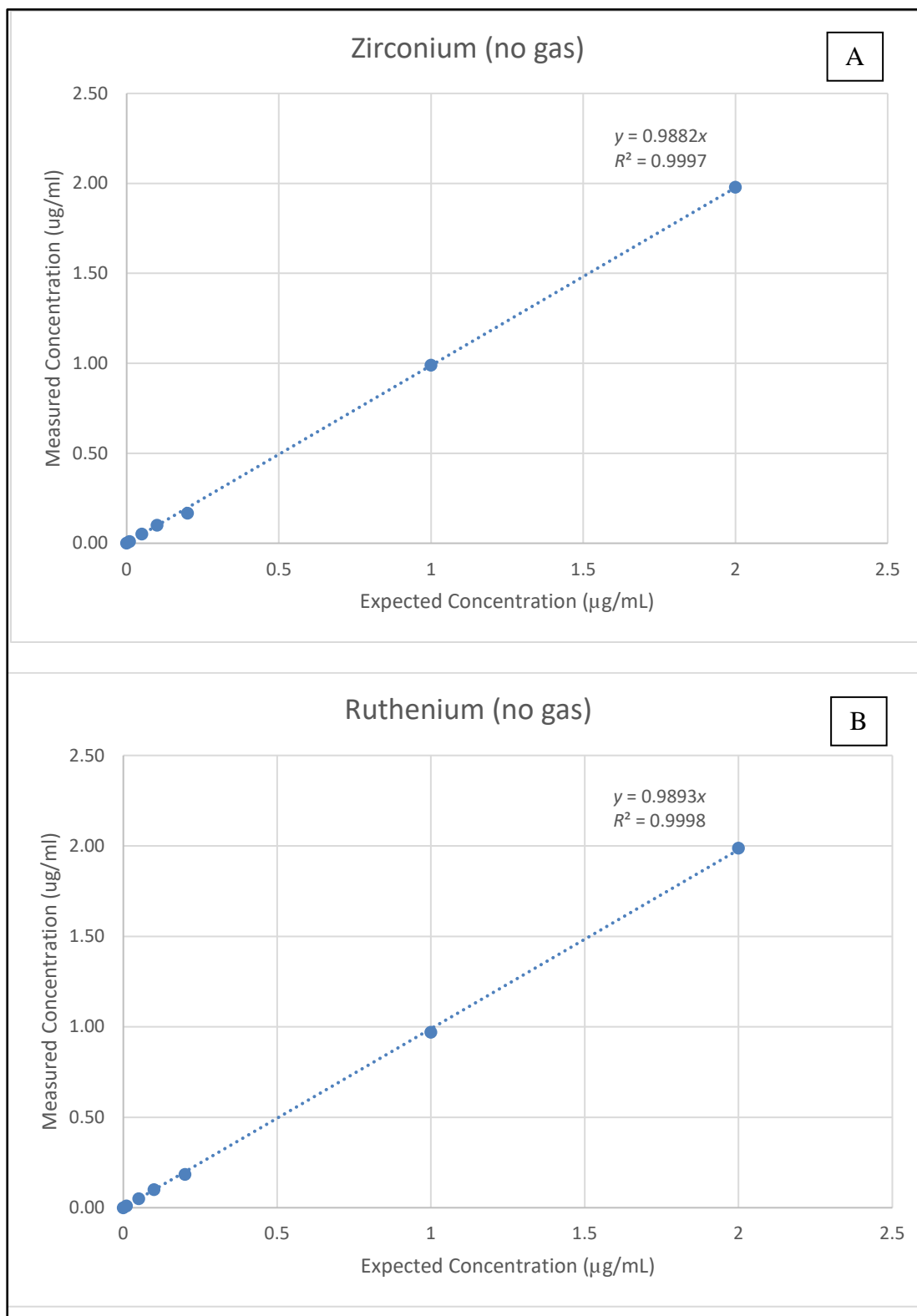| Analyte		Concentration Range (ppm)
No.	Isotope	
1	^{40}Zr	0.01–2.0
2	^{44}Ru	0.01–2.0

Figure 1. Isotopes (A) zirconium-40 and (B) ruthenium-44 calibration curves from 0 to 2 ppm.

4.2   Relative Percent Differences

The precision of the analysis of the samples is determined by calculating the relative percent difference between the measured and expected concentrations:

$$\left(\frac{C_M - C_E}{\text{Average } (C_M + C_E)} \right) \times 100\% \tag{3}$$

where C_M is the concentration measured by the instrument, and C_E is the expected concentration.

Each ion had a minimum of five valid points in the calibration curve (Table 2).

4.3   Method Detection Limits (MDLs)

An MDL was performed as described in Chapter 1 of EPA Publication SW-846.[5] Five replicate solutions with all analytes were prepared by spiking the matrix with the analyte at a concentration equal to three to five times the estimated MDL. The solutions were analyzed in random order. Each element was spiked at 0.005 ppm. The MDL was determined by multiplying the appropriate one-sided 99% t statistic (2.57 for six measurements) by the standard deviation (SD) of the replicate measurements:

$$\text{MDL} = 2.57 \times \text{SD} \tag{4}$$

The MDLs for the analytes are listed in Table 4.

Table 4. MDLs for All Analytes

Sample ID		SD	MDL (ppm or μg/L)
No.	Isotope		
1	^{40}Zr	0.00118	3.95
2	^{44}Ru	0.0000681	3.93

4.3.1   Precision and Accuracy Study

Three solutions at each calibration level were prepared and analyzed in random order. This procedure was repeated on a second day to prepare a separate batch of standards at each level for a total of six analyses at each calibration level. Concentrations of the tested calibration levels are listed in Table 5.

**Table 5. Concentrations of Calibration Solutions Used
for Precision and Accuracy Levels**

Level	Concentration (µg/mL)		
	Target	**Day 1**	**Day 2**
1	0.01	0.01	0.01
2	0.05	0.0499	0.0497
3	0.1	0.100	0.103
4	0.2	0.199	0.198
5	1.0	1.00	1.00
6	2.0	1.99	2.01

The relative standard deviation (RSD) of the three solutions at each calibration level was calculated using eq 4, as follows:

$$RSD = \left(\frac{SD \text{ of replicates}}{\text{average result}}\right) \tag{5}$$

Percent recoveries were 90% or greater for zirconium and ruthenium (Tables 6 and 7).

Table 6. Precision and Accuracy for Zirconium across Six Levels

Level or Parameter	Recovered Concentration (µg/mL)					
	[0.01]	**[0.05]**	**[0.1]**	**[0.2]**	**[1.0]**	**[2.0]**
Replicate 1	0.0098	0.0516	0.102	0.204	1.026	2.057
Replicate 2	0.012	0.0517	0.104	0.204	1.029	2.024
Replicate 3	0.0098	0.0522	0.103	0.206	1.026	2.036
Replicate 4	0.009	0.0477	0.0934	0.191	1.002	2.013
Replicate 5	0.0091	0.0442	0.0945	0.187	1.012	2.015
Replicate 6	0.018	0.0436	0.0938	0.187	0.999	2.013
SD	0.0033	0.00392	0.00498	0.00911	0.0132	0.0175
Average	0.011	0.0485	0.0984	0.196	1.0157	2.026
% Recovered	112.83	97.0000	98.383	98.192	101.567	101.317
% CV	29.55	8.075	5.063	4.641	1.298	0.861

Note: Square brackets indicate calibration solution concentration.

Table 7. Precision and Accuracy for Ruthenium across Six Levels

Level or Parameter	Recovered Concentration (µg/mL)					
	[0.01]	**[0.05]**	**[0.1]**	**[0.2]**	**[1.0]**	**[2.0]**
Replicate1	0.0101	0.0502	0.101	0.201	1.001	2.06
Replicate 2	0.0097	0.0505	0.103	0.201	1.003	2.029
Replicate 3	0.0097	0.05	0.101	0.202	1.003	2.049
Replicate 4	0.0109	0.0492	0.103	0.201	1.107	1.964
Replicate 5	0.0109	0.0456	0.102	0.205	1.118	1.973
Replicate 6	0.0109	0.0461	0.102	0.202	1.11	1.959
SD	0.000602	0.00218	0.000751	0.00170	0.06	0.0455
Average	0.01037	0.0486	0.102	0.2018	1.057	2.006
% Recovered	103.667	97.2	102	100.875	105.7	100.283
% CV	5.8092	4.484	0.736	0.843	5.676	2.269

Note: Square brackets indicate calibration solution concentration.

4.3.2   Measurement of Uncertainty

The measurement uncertainty for the three solutions at each calibration level was determined in accordance with ECBC FAC work instruction WI-091.[4] The major sources contributing to the measurement of uncertainty were errors from the calibration curve and process repeatability. These sources were measured during the method validation and then combined to determine the overall uncertainty at 95% confidence (Table 8).

Table 8. Measurement of Uncertainty

Analyte	Concentration (µg/mL)	Uncertainty (%)
Zirconium	0.01	131
	0.05*	28
	0.1	16
	0.2	13
	1.0	4
	2.0	2
Ruthenium	0.01	291
	0.05*	59
	0.1	29
	0.2	15
	1.0	16
	2.0	6

*Denotes practical quantitation limit identified through precision and accuracy and measurement uncertainty.

5.   CONCLUSIONS

       ICP–MS is a viable method for qualitative and quantitative analyses of two analytes in aqueous solution. Calibration curves were valid for a minimum of five points for all analytes. MDLs were calculated for zirconium and ruthenium. Measurements of uncertainty were also calculated for zirconium and ruthenium at each calibration level.

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ACRONYMS AND ABBREVIATIONS

ECBC	U.S. Army Edgewood Chemical Biological Center
FAC	Forensic Analytical Center
ICP–MS	inductively coupled plasma mass spectrometry
IEC	International Electrotechnical Commission
ISO	International Organization for Standardization
MDL	method detection limit
MOF	metal organic framework
PP	polypropylene
RSD	relative standard deviation
SD	standard deviation

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